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A DISSERTATION SUBMITTED TO THE FACULTY OF THE DIVISION OF THE PHYSICAL SCIENCES IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

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The Abundance Ratio of the Isotopes in Natural or Isotopically Separated Carbon

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(Received June 19, 1937)

The relative intensity of the 1,0 band heads of the $C_{12}C_{12}$ and $C_{12}C_{13}$ molecules in the Swan system of the C_2 spectrum has been measured by a photographic spectrophotometric method and found to be 0.0217 ± 0.0009. This yields a value of 92.2 ± 3.7 for the C_{12}/C_{13} abundance ratio of the carbon isotopes in good agreement with the value reported by Vaughan, Williams and Tate (91.6 ± 2.2), from mass-spectrographic data. This work was done in connection with the development of a simple method suited to the determination of the abundance ratio in the small samples obtained in the separation of natural carbon into isotopes. This method is described.

I. Introduction

THE purpose of the work reported here was to obtain a simple method to be used in following the extent of separation of carbon into isotopes. By the use of this modified and improved form of the spectroscopic method used by Jenkins and Ornstein[1] the abundance ratio of C^{12} and C^{13} in natural carbon has been determined. This method is extremely easy and simple if the band spectra employed are obtained by the use in the discharge tube of an unsaturated hydrocarbon. Thus acetylene, which contains one atom of hydrogen to one of carbon gives excellent results and is easily prepared. However, if the oxides of carbon or saturated hydrocarbons are used in an isotopic separation, it is difficult to convert the small quantity obtained in some of the fractions into acetylene or even ethylene. On this account methane, a saturated hydrocarbon, which may be easily prepared from any carbon compound, was used, and the spectroscopic difficulties due to an excess of hydrogen were overcome by the method described later.

Values for the abundance ratio of the carbon isotopes and for the chemical atomic weight of carbon which have been reported recently show variations which are larger than would be expected to result from isotopic separation during the preparation and purification of carbon compounds. Jenkins and Ornstein[1] in a study of the relative intensity of the 1,0 band heads of $C_{12}C_{13}$ and $C_{12}C_{12}$ in the Swan system of C_2 concluded that this intensity ratio (0.019 ± 0.002) was independent of the method of excitation and proportional within two or three percent[2] to the abundance ratio of the isotopes. They gave 106 for the ratio C_{12}/C_{13}. In a mass-spectrographic study of the abundance ratios of the isotopes of the lighter elements Aston[3] reported 140 ± 14 for the C_{12}/C_{13} ratio. Vaughan, Williams and Tate,[4] gave 91.6 ± 2.2 for this ratio.

II. Apparatus and Procedure

As in the work of Jenkins and Ornstein[1] the relative intensity of the 1,0 band heads of the Swan systems of $C_{12}C_{12}$ and $C_{12}C_{13}$ at $\lambda4737$ and $\lambda4744$, respectively, was measured by a photographic spectrophotometric method. The apparatus used in the excitation of the Swan system of the C_2 spectrum is shown in Fig. 1. The discharge tube *D* was made of Pyrex glass with a capillary restriction 1.5 mm in diameter and 5 cm in length. The cylindrical electrodes were made of 16 gauge (B & S) nickel wire wound into a tight coil 15 mm long and 15 mm in diameter. They were 12 cm apart and were connected to the external electrical circuit through Pyrex-tungsten seals. The discharge was maintained by a 0.44 kva Thordarson transformer *H* which supplied 15,000 volts maximum, a 0.04 mf condenser *I* and an adjustable spark gap *J*.

The Swan system of the C_2 spectrum was obtained with great intensity when the discharge tube contained methane at a pressure of about 0.25 mm of mercury and helium at a pressure of 16 mm. Helium was used to lower the effective temperature of the C_2 bands thereby increasing

[1] Jenkins and Ornstein, Proc. Amst. Acad. Sci. **35**, 1212 (1932).

[2] Dunham, Phys. Rev. **36**, 1553 (1930).

[3] Aston, Proc. Roy. Soc. (London) **A149**, 400 (1935).

[4] Vaughan, Williams and Tate, Phys. Rev. **46**, 327 (1934).

the intensity of the 1,0 band head relative to the background intensity and at the same time suppressing the overlapping tails of the bands of the zero sequence. With helium pressures below 12 mm or methane pressures above 0.5 mm reliable intensity measurements could not be made because of overlapping of the zero sequence. With helium pressures above 20 mm or methane pressures much below 0.1 mm the intensity of the Swan system was greatly reduced.

Harkins and Jackson[5] in work done in this laboratory found that in the glow discharge through methane the C_2 bands disappeared altogether and the molecular spectrum of hydrogen became very strong. In this work the intensity of the C_2 spectrum was maintained by removing H_2 through the palladium valve *C* (Fig. 1). This was made from a palladium tube 3 mm in diameter and 4 cm long connected to the discharge tube through Pd-Pt and Pt soft glass seals and a soft glass Pyrex ground glass joint. It was heated by a tungsten filament insulated from the Pd by a thin sheet of mica. Hydrogen was pumped continuously from the bulb surrounding the valve with a mercury vapor pump and a Cenco Hyvac fore pump. The hydrogen molecular spectrum was further suppressed by introducing sulfuric acid[6] into the bulb *E*.

During an exposure the discharge was observed through a small spectrometer. When the decomposition of methane progressed to the stage where the intensity of the C_2 spectrum began to decrease methane was admitted from the reservoir *G* to the chamber of known volume *F* and from there to give a known pressure in the discharge tube.

A charcoal trap *B* immersed in liquid nitrogen was used to purify helium and to outgas the electrodes. This was done by running the discharge for three hours through 20 mm of helium with the charcoal trap in communication with the discharge tube.

When an unsaturated hydrocarbon with a low hydrogen to carbon ratio was used as a source of carbon it was no longer necessary to remove hydrogen through the palladium valve. It was found, however, that the introduction of sulfuric

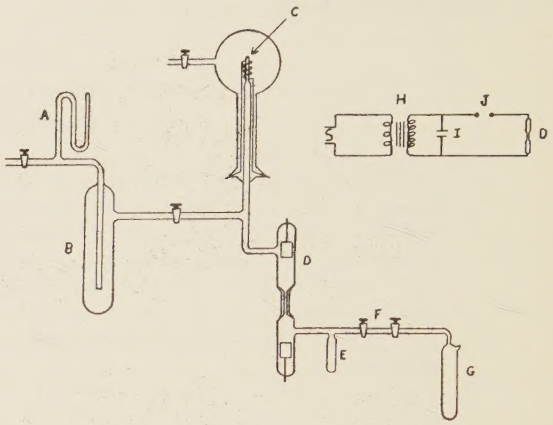

FIG. 1. Apparatus used to obtain the 1,0 band heads of the $C_{12}C_{12}$ and $C_{12}C_{13}$ spectrum.

acid into the bulb *E* greatly enhanced the C_2 spectrum in this case. An unsaturated hydrocarbon was not used in this work because of the difficulty in converting small amounts of methane or the oxides of carbon, which are most usually obtained as final products in isotopic separations, into an unsaturated hydrocarbon.

The oxides of carbon could not be used as a source of C_2 because it was found impossible to suppress the overlapping λ4835 band of carbon monoxide sufficiently.

The methane used in all of the experiments reported in this paper was made by reducing tank carbon dioxide with hydrogen over a nickel catalyst.[7] It was purified by repeated fractional distillation.

The C_2 spectrum was photographed through the side of the capillary of the discharge tube with a Hilger E1 spectrograph. In order to obtain sufficient definition it was necessary to keep the temperature of the instrument constant within ±0.5°C for at least an hour before and during the exposure which usually lasted about one hour. A photographic step weakener was placed immediately before the slit to obtain density marks for the calibration[8] of the plates.

The step weakener was made from an Eastman lantern slide plate exposed to give densities with transmissions decreasing in an approximately geometric ratio. A protective glass cover was

[5] Harkins and Jackson, J. Chem. Phys. **1**, 37 (1933).
[6] Smallwood, J. Am. Chem. Soc. **56**, 1542 (1934).
[7] Hightower and White, Ind. and Eng. Chem. **20**, 10 (1928).
[8] Harrison, J. Opt. Soc. Am. **19**, 267 (1929); **24**, 59 (1934).

TABLE I. *Intensity ratio of band heads.*

PLATE	INTENSITY RATIO λ4744/λ4737	DEVIATION FROM MEAN
11	0.0222	0.0005
14	0.0237	0.0020
15	0.0220	0.0003
17	0.0207	0.0010
18	0.0217	0.0000
19	0.0202	0.0015
Average	0.0217	0.0009

cemented to the emulsion side of the plate with Canada balsam. The weakener had six steps 2 mm wide and 3 cm long with clear portions at each end which made it possible to detect and correct for any intensity gradient which might exist along the slit.

The transmissions of the weakener steps at λ4740 were measured by three different methods: (1) By placing the weakener behind a slit in a parallel beam in the photoelectric spectrophotometer described by Hogness, Zscheile and Sidwell.[9] A narrow band 10A on each side of λ4740 was used in comparing the transmissions of the separate steps with the clear portions of the weakener. (2) By placing the weakener immediately before the slit in a photoelectric photometer of the type described by Dershem.[10] A combination of Jena glass filters BG7 and GG5 was placed between the source and the weakener. (3) The spectrum of a constant and continuous source was photographed with equal periods of exposure through the weakener and through a step sector rotating at 1800 r.p.m. on the same plate. From the densities produced through the sector a calibration curve was drawn for the plate at λ4740. The transmissions of the weakener steps were then obtained by reading the intensities corresponding to the densities produced through the weakener from the calibration curve. The transmissions obtained by the three methods agreed within two percent.

[9] Hogness, Zscheile and Sidwell, J. Phys. Chem. **41**, 379 (1937).
[10] Dershem, Rev. Sci. Inst. **3**, 43 (1932).

TABLE II. *Values of C_{12}/C_{13} ratio recently reported.*

REFERENCE	METHOD	C_{12}/C_{13}
1	Band Spectrum Intensities	106 ±11
3	Mass-Spectrographic Data	140 ±14
4	Mass-Spectrographic Data	91.6± 2.2
This work	Band Spectrum Intensities	92.2± 3.7

The Eastman 33 plates used in this work were developed in Rodinal one part water twenty parts for five minutes at 18°C using rocked tray technique. They were thoroughly fixed, washed and dried in a dust free atmosphere.

The plates were photometered on a photoelectric photometer of the type described by Dershem.[10] A separate calibration curve was constructed for each plate from the densities of the λ4737 band head in the weakened portions and the relative intensities of the λ4744 isotopic band head and background in the unweakened portion were read from the calibration curve. The data given in Table I involve the assumptions that the background intensity is constant over the region from λ4750 to λ4737 and that fogging from the $C_{12}C_{12}$ band head at λ4737 in the unweakened portion does not extend to λ4744.

III. RESULTS

The average intensity ratio λ4744/λ4737 from six plates (0.0217±0.0009) gives 92.2±3.7 for the C_{12}/C_{13} abundance ratio. This is in good agreement with the ratio obtained by Vaughan, Williams and Tate from mass-spectrographic data. Recently reported values for this ratio are tabulated in Table II.

With values for the physical atomic weights of C_{12} and C_{13} as determined from mass-spectrographic[11] and nuclear disintegration[12] data and 1.00025 for the conversion factor[13] from the chemical to the physical system gives 12.011_2 ±0.0005 for the chemical atomic weight of carbon.

[11] Aston, Nature **137**, 357 (1936); **139**, 922 (1937).
[12] Oliphant, Nature **137**, 396 (1936).
[13] Smyth, Phys. Rev. **45**, 299 (1934).

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